

PATENT SPECIFICATION

597,144



Convention Date (United States of America): Sept. 29, 1944.

Application Date (in United Kingdom): Sept. 18, 1945. No. 24103/45

Complete Specification Accepted: Jan. 19, 1948.

COMPLETE SPECIFICATION

Improvements in or relating to Synthetic Resinous Adhesive Compositions

WE, WESTINGHOUSE ELECTRIC INTERNATIONAL COMPANY, of 40, Wall Street, New York, 5, State of New York, United States of America, a Corporation organised and existing under the Laws of the State of Delaware in said United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to synthetic resinous compositions for bonding members and more particularly for bonding metal plates to one another, and the product produced by the use of such resinous bonding materials.

It has been long held desirable to bond sheets of metal by adhesive compositions in order to produce consolidated bodies for various applications. In the electrical industry, it is highly desirable to prepare magnetic cores from laminations of magnetic iron. For ease in manufacturing and assembly, adhesively bonded magnetic cores have considerable advantages.

It has been proposed heretofore to apply thermoplastic resinous binders between laminations of metal in order to produce a bonded core therefrom. However, the thermoplastic resin lacks adequate bond strength at reasonable elevated operating temperatures and the cores tend to delaminate at temperatures much below expected operating temperatures. Thermosetting resins such as, for example, a phenolformaldehyde on the other hand have been found unsatisfactory since they induce strains in the magnetic material on heat hardening and thereby greatly impair the magnetic characteristics of the material. In some cases thermosetting resins lack adequate bond strengths.

The chief object of this invention is to provide a resinous binder for application to metallic laminations for preparing bonded bodies therefrom.

A further object of the invention is to provide a body composed of laminations bonded with a resinous binder capable of maintaining a good bond at elevated tem-

peratures.

Another object of the invention is to provide a magnetic core composed of laminations bonded with a resinous binder capable of maintaining a good bond at elevated temperatures without impairing the magnetic properties of the metal.

A still further object of the invention is to provide for building cores of metal sheets by applying thereto to resin composition comprising a resorcinol-formaldehyde reaction product and a thermoplastic vinyl resin.

With the above objects in view the present invention resides in a synthetic resin, particularly for use as a binder for metal sheets and the like, characterised in that the composition comprises essentially from 10 to 100 parts by weight of a soluble partial reaction product of from 1 to 1.17 mols of formaldehyde and 1 mol of a polyhydroxy benzene having at least two hydroxyl groups in the 1, 3, 5 positions, refluxed in substantially anhydrous methanol and a catalyst in an amount of less than 1% of the weight of the polyhydroxy benzene, the catalyst being neutralised after the reaction, and 100 parts by weight of a compatible thermoplastic vinyl resin selected from the polymers of compounds having the radical $H_2C=C<$.

It has been discovered that a binding agent prepared from a resorcinol-formaldehyde resin combined with from 1 to 10 times its weight of a thermoplastic vinyl type resin gives extraordinarily strong bonds when applied to metal and maintains a high bond strength at temperatures of 100°C. and higher. Furthermore, the binding agent does not induce strains or otherwise cause significant losses in magnetic laminations bonded therewith.

In preparing the binding agents of this invention, from 10 to 100 parts by weight of the reaction product of a 1, 3, 5 dihydroxybenzene having hydrogen atoms attached to the remaining carbon atoms except that a single methyl, ethyl or other group may be attached to the benzene ring or a 1, 3, 5 hydroxy benzene hav-

[Price 2/-]

ing only hydrogen on the remaining carbon atoms reacted with formaldehyde are combined with 100 parts by weight of a vinyl type thermoplastic resin. By "vinyl type resins" as used herein is meant the class of resins obtained by polymerising organic compounds having the radical $H_2C=C<$. The vinyl type resin may be selected from the vinyl esters such, for example, as vinyl acetate and vinyl acetate-butyrate, polyvinyl alcohols particularly those produced from a vinyl ester hydrolyzed less than 50%, polyvinyl formal, polyvinyl acetal and polyvinyl butyral, and simple substituted vinyls such, for example, as the acrylates and methacrylates. Specific examples of the two vinyl derivatives last-mentioned are methyl methacrylate and propyl methacrylate. The vinyl resins may be of low-medium and high molecular weight, depending on the desired hardness, toughness and tackiness of the bond.

The polyhydroxy benzenes are reacted with formaldehyde under anhydrous conditions in order to provide a complete control of the reaction in order to secure predetermined properties. The reaction is particularly controllable if carried out in a liquid medium composed of substantially anhydrous methanol and ethanol.

EXAMPLE A.

The following example is typical of the method of preparation. Into a reaction vessel equipped with a mechanical stirrer and condenser 220 parts by weight of resorcinol and 70 parts of paraformaldehyde by weight are mixed in 250 parts of 99.7% methyl alcohol. One-half part by weight of concentrated hydrochloric acid is added as a catalyst. Heat is applied to the mixture while being rapidly stirred. The reaction temperature is brought to the reflux point of the alcohol (about 75°C.) and gradually decreased thereafter to about 68°C. During the heating process, the milky colour due to the paraformaldehyde being suspended in the methyl alcohol disappears in about 20 minutes. The resin solution is quite viscous but clear. Heating is discontinued when this condition occurs, and the resin solution cooled. Sufficient additional methyl alcohol is added to the resin solution, to provide a solution of the proper viscosity for use. Sufficient alkali is added to neutralize the acid. The resulting solution has been stored for periods of eight months and longer without any appreciable change in viscosity or other properties.

EXAMPLE B.

In another example nearly absolute anhydrous ethyl alcohol was used as the solvent and reaction medium instead of

methyl alcohol. The time of reaction was somewhat shorter in this latter case since the boiling point of ethyl alcohol is somewhat higher and the higher reflux temperature expedited reaction. A resin solution having excellent adhesive properties when admixed with a vinyl resin and good stability was produced.

It is believed that the substantially anhydrous alcohol has a greater affinity for the water of condensation than the resinous product, and, therefore, the resin proper is substantially free of water.

In order to provide good controllability of the reaction, the amount of catalyst should be less than 1% of the weight of the reactants, preferably one-fourth of 1% and less. When the reaction has reached the stage where the formaldehyde and polyhydroxy benzene are reacted and the resin molecules are of a size whereby predetermined viscosity of solution is attained, the addition of cold monohydric alcohol will reduce the temperature sufficiently to practically terminate any further reaction tending to increase the molecule size. The catalyst is neutralized by adding the appropriate alkali or acid substance to convert the catalyst into an inert residue.

Suitable 1, 3 and 1, 3, 5 polyhydroxy benzenes for carrying out the invention are resorcinol and phloroglucinol. 1, 3 polyhydroxy benzenes with one ethyl, methyl, or other group attached to the benzene ring may be employed.

Catalysts suitable for the reaction are the mineral acids. Salts which give a strong acidic reaction, such for example, as ferric chloride, also may be employed. Basic catalysts will be found to be operative as well.

Paraformaldehyde is the preferred form of aldehyde due to ease of handling. The mol ratios of polyhydroxy phenol to formaldehyde to produce resins suitable for good thermoset products preferably ranges from 1 to 1.17 mols of formaldehyde to each mol of the polyhydroxy phenol. A slight molar excess of the aldehyde over the moles of the polyhydroxy benzene gives better results.

The following are examples of the preparation of a binding composition:—

EXAMPLE I.

67 parts by weight of a resorcinol resin solution in methanol as produced in Example A having a 60% solids content is mixed with a solution composed of 200 parts by weight of polyvinyl acetate of medium molecular weight dissolved in 400 parts by weight of acetone. The composition is ready for application to laminations of metal immediately on

thorough mixing.

EXAMPLE II.

27 parts by weight of resorcinol-formaldehyde resin dissolved in methanol as produced in Example A to a 60% solids content is combined with 200 parts by weight of a solution composed of 40 parts by weight of a high molecular weight polyvinyl acetate in 160 parts by weight of acetone. The composition is ready for use after thorough mixing.

EXAMPLE III.

400 parts by weight of low molecular weight polyvinyl acetate was dissolved in 400 parts by weight of benzene mixed with 400 parts by weight of ethanol and to the solution 600 parts by weight of a 60% solid content resorcinol-formaldehyde resin in ethanol as in Example B was added.

In Examples I. to III. above, a basic catalyst may be added to the composition in amounts of up to 10% of the weight of the resorcinol-formaldehyde resin present. Suitable catalysts are ammonium hydroxide, ethylene-diamine and hexamethylenetetramine. Such basic catalysts will lower the baking times and temperatures required to set the binding agent when applied to laminations of metal.

EXAMPLE IV.

Three parts of 15% hydrolysed polyvinyl acetate, medium molecular weight, dissolved in a mixture of equal parts of acetone and ethyl acetate to produce a 20% solution was combined with one part of resorcinol-formaldehyde resin dissolved in ethanol as in Example B to produce a 50% solution.

The invention will become more readily apparent from the following description of preferred embodiments thereof shown by way of example in the accompanying drawing.

Figure 1 is a perspective view of a bar core;

Fig. 2 is an exploded perspective view of two U-shaped core segments;

Fig. 3 is an enlarged cross sectional view taken along line III-III of Fig. 2; and

Fig. 4 is a graph plotting bond strength against temperature.

Referring to Fig. 1 of the drawing, there is illustrated a bonded core 10 composed of a plurality of laminations of magnetic sheets 12 bonded by applying thereto the composition described in Example I. The laminations were individually coated with the composition and allowed to dry either by exposure to the atmosphere or placed in ovens at a temperature of 80°C. After drying, the laminations were super-imposed on one another to form a stack and the stack was

placed in a jig where a pressure of some 10 to 100 pounds per square inch (0.7 to 7 kg per cm²) could be applied. The stack was then baked in an oven for four hours at a temperature of 150°C. to 250°C. If a basic catalyst is employed in combination with an adhesive, these baking times may be reduced. The baked cores after cooling to temperatures at which they could be handled can be machined to predetermined size and shape. The machining operations may consist of milling, drilling, grinding and the like. In making magnetic cores, it may be desirable to etch the machined core 10 in order to remove burrs and metal particles that may short circuit the laminations. Etching in nitric acid for a few minutes has been found satisfactory for this purpose. The bond between laminations withstands the action of the acid and subsequently applied alkalies and water for neutralizing excess acid.

An advantageous application for the bonding compositions of this invention is in the making of the wound magnetic core 20 shown in Fig. 2 of the drawing. The core 20 is prepared by winding a continuous strip of magnetic sheet about a rectangular mandrel. The continuously wound core enables an efficient use of magnetic material having a preferred direction of magnetic orientation. After the core has been wound into a rectangular body, it is strain annealed to remove the winding strains and when cool it is submerged in the bonding composition described herein. The resinous composition will penetrate the spaces between the windings 26. To insure thorough impregnation, the wound core may be placed in a vacuum impregnating tank where a low vacuum is applied to remove any gases between the turns of the core and thereafter the binding agent solution is admitted to immerse the cores in the tank. Pressure may be applied to as high a value as 100 pounds per square inch (7 kg per cm²) to force the composition into the spaces between the laminations 26. The composition may be drained from the cores after 30 minutes and a slight vacuum applied to remove excess adhesive composition. The wound and impregnated cores may be placed in jigs in order to maintain predetermined shape and baked at temperatures of up to 250°C. for several hours to polymerize and harden the composition. After cooling to room temperature the baked cores are removed from the jigs and may be cut by means of a milling cutter, saw, or thin grinding wheel into two U-shaped magnetic cores 22 and 24. The faces 28 may be ground and etched to put them into 130

a flat planar shape and to remove burrs and other short-circuiting particles. Nitric acid etch, for example, is satisfactory for this purpose. After etching, 6 excess acid may be washed off with alkalis and water.

As shown in the greatly enlarged view in Fig. 3 of the drawing, the laminations 26 are impregnated and cemented to 10 together by the resin composition 30 between the respective laminations. A high degree of resin filling between laminations is present.

The temperature characteristics of the bond composition are outstanding. Referring to Fig. 4 of the drawing, there is a plot of bond strength in pounds (kg) for an area of 5.25 square inches (33.86cm²) for a range of temperatures from 25°C. 20 to 100°C. At room temperature, approximately 25°C, the bond strength is about 2750 pounds (1247.40kg). A 60°C. the bond strength has increased approximately over 50% to about 4200 pounds 25 (1905.12kg). At 80°C. the bond strength is 2500 pounds (1134kg) while at 100°C. the bond strength is 1450 pounds (657.72kg). An all vinyl resin bond by comparison has a maximum bond strength at 25°C. of 2500 pounds (1134kg) for an 30 area of 5.25 square inches (33.86cm²). This value diminishes to 1,000 pounds (453.6kg) at 60°C. and there is no bond strength at 80°C.

35 Cores similar to those shown in Fig. 2 of the drawing have been prepared by means of the bonding composition of this invention. When the cores were tested the change in magnetic losses is approximately 0.8% as an average for a large 40 number of cores. This loss is well within the accuracy of the testing devices employed. It indicates that the composition employed as the binder does not induce 45 appreciable strains in the laminations bonded therewith. This feature of low losses is particularly significant in making cores with magnetic sheets having a preferred direction of magnetization. 50 This type of material is extremely sensitive to any strains. Ordinary phenol formaldehyde resin usually increases the losses when applied to laminations of oriented magnetic sheets 20 to 30% 55 and even higher.

A particular advantage secured by the use of the binding composition of this invention resides in the toughness of the bond. The removal of mandrels from 60 cores after annealing and the cutting and grinding operations subject the cores to considerable physical stresses and the

laminations would break and separate if the bond were brittle. The present composition, however, is so tough that it withstands the machining and other manufacturing operations encountered with substantially no splitting of the cores or other failures.

While the bonding composition of this invention exhibits its most desirable properties in the manufacturing of magnetic cores, the composition may be employed for bonding metallic members of any variety, wood and laminated plastics. 70 The bonded materials may be cut, drilled and machined to shape in much the same manner as a solid body of the material could normally be machined.

The resinous composition after heat 80 treatment to polymerize and harden it is impervious to oil, water and fluid dielectrics at temperatures of the order of 100°C. This renders cores bonded therewith usable in various dielectric fluids. 85

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:— 90

1. A synthetic resin, particularly for use as a binder for metal sheets and the like, characterized in that the composition comprises essentially from 10 to 100 parts by weight of a soluble partial reaction product of from 1 to 1.17 mols of formaldehyde in the form of a solid polymer and 1 mol of a polyhydroxy benzene having at least two hydroxyl groups in the 1, 3, 5 positions, refluxed in substantially anhydrous methanol or ethanol and a catalyst in an amount of less than 1% of the weight of the polyhydroxy benzene, the catalyst being neutralized after the reaction, and 100 parts by weight of a compatible thermoplastic vinyl resin selected from the polymers of compounds having the radical $H_2C=C<$. 95

2. A composition as claimed in claim 1, characterized by the addition of methanol to the polyhydroxy benzene compound-formaldehyde reaction product. 100

3. A composition, as claimed in claim 1 or 2, characterized in that the polyhydroxy benzene compound is resorcinol. 105

4. A composition, as claimed in any of the preceding claims, characterized in that the thermoplastic vinyl resin consists of polyvinyl acetate. 110

5. The synthetic resinous composition 120 particularly for use as a binder for metal sheets and the like, substantially as hereinbefore described.

Dated the 17th day of September, 1945.

G. RAYMOND SHEPHERD,
Chartered Patent Agent,
2, Norfolk Street, Strand, London, W.C.2,
Agent for the Applicants.

London: Printed for H. M. Stationery Office, by Charles & Read Ltd. - 1951.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies, price 2s 0d. per copy, by post 2s. 1d., may be obtained.

[Second Edition.]

Fig. 1.



Fig. 2.

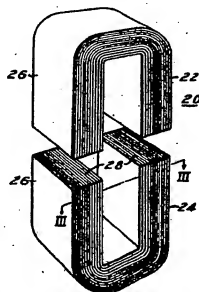


Fig. 3.

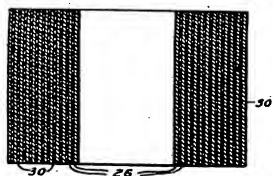
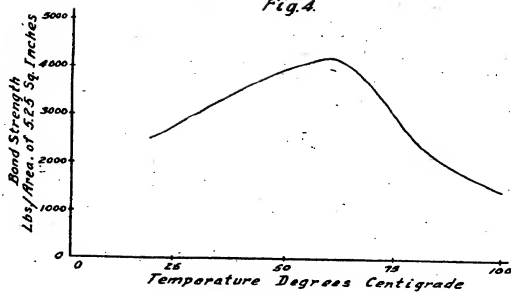


Fig. 4.



Charles & Read Ltd.

[This Drawing is a reproduction of the Original on a reduced scale.]